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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Process of Purifying an H<sub>2</sub>S- and CO<sub>2</sub>-Containing Gas

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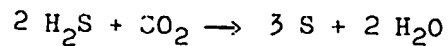
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This invention relates to a process of purifying a gas which contains combustible components as well as carbon dioxide and sulfur compounds, particularly  $H_2S$ , in that the gas is scrubbed in a scrubbing zone with a scrubbing solution, which is regenerated and re-used, wherein the scrubbing solution to be regenerated is pressure-relieved, stripped, and heated in a hot regenerating zone, an exhaust gas rich in  $H_2S$  produced in the hot regenerating zone is processed to form elementary sulfur and a residual gas which contains  $H_2S$ , and the residual gas is contacted with scrubbing solution.

European Patent O 054 772 describes a process which is of that kind and in which the exhaust gas that is supplied to the Claus process plant contains considerable amounts of  $CO_2$  in addition to  $H_2S$ . That exhaust gas is processed further in a relatively expensive Claus process plant, which includes two or three

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catalytic stages, in which after a partial combustion of  $H_2S$  to  $SO_2$  the exhaust gas is catalytically converted as completely as possible to elementary sulfur and water by the Claus reaction



Before and behind each of said catalytic stages, elementary sulfur is condensed from the mixed gases and is removed. In the known process the catalytic conversion stages are succeeded by a hydrogenation and the exhaust gas is thereafter recycled to the scrubber.

Those catalytic processing stages give rise to considerable costs and have the disadvantage that they render the start-up of the plant from standstill expensive and time-consuming. There is also a risk that in case of frequent start-ups and shutdowns and of extreme load changes the catalysts will soon lose their activity.

It is an object of the invention so to process the exhaust gas rich in  $H_2S$  that is formed in the hot regenerating zone that a fast start-up from a standstill can be effected in a simple manner and even a frequent load change will not be problematic. In the process which has been described first hereinbefore this is accomplished in accordance with the invention in that the exhaust gas which is rich in  $H_2S$  and has been produced in the hot regenerating zone is

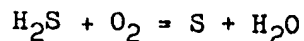
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partly combusted in a combustion chamber with oxygen, oxygen-containing gas or air; a gas mixture which is at a temperature in the range from 1000 to 2000°C and in which <sup>at least</sup> 30 mole percent of the sulfur supplied to the combustion chamber are contained as elementary sulfur and which also contains the components  $H_2S$  and  $SO_2$  in a molar ratio of 4:1 to 1:1 is produced in the combustion chamber; <sup>the</sup> gas mixture is cooled below the dew point temperature of sulfur; condensed elementary sulfur is removed; the gas mixture is subsequently heated to temperatures of 180 to 280°C and is then directly subjected to a catalytic hydrogenation and/or hydrolysis, whereby the residual content of  $SO_2$  is substantially converted to  $H_2S$  ;

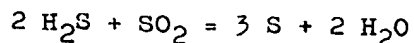
and at least part of the gas which has thus been treated is contacted as an  $H_2S$ -containing residual gas with scrubbing solution. The process in accordance with the invention is particularly desirable for the desulfurization of fuel gases to be used as fuel in a gas turbine-steam turbine power plant.

In the process in accordance with the invention, care is taken to ensure that the gas which is rich in  $H_2S$  and supplied to the combustion chamber is highly enriched with  $H_2S$  so that a large share of the hydrogen sulfide is reacted to elementary sulfur by the reaction

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in and immediately after the combustion chamber and there is no longer a need for a further processing of the gas mixture by a catalytic reaction of  $\text{H}_2\text{S}$  and  $\text{SO}_2$  according to the Claus reaction



A reaction of  $\text{H}_2\text{S}$  to a lower degree is intentionally tolerated and this will also increase the demand for hydrogen for the hydrogenation. But in the process in accordance with the invention the higher rate of hydrogenation requires that the hydrogenation catalyst is cooled and in the process in accordance with the invention that cooling can be effected by the feeding of a cooling gas, which may also be used to supply the deficient hydrogenating hydrogen.

The residual gas which is high in  $\text{H}_2\text{S}$  and has been produced in the hydrogenating and/or hydrolyzing stage may be recycled, e.g., to the scrubbing zone or to the regenerating stage. Alternatively, part of that residual gas may directly be supplied to the combustion chamber and this will be recommendable particularly if oxygen and an exhaust gas which is highly enriched with  $\text{H}_2\text{S}$  are supplied to the combustion chamber.

The hot regeneration produces an exhaust gas which has a low  $\text{CO}_2$  content not in excess of 10% by volume or will have a much lower  $\text{CO}_2$  content if the laden scrubbing solution from the scrubbing zone is pressure-relieved in at least two regenerating columns

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before the hot regeneration. In that case it will be recommendable to feed at least part of the flashed-off gas as a stripping gas to the preceding stage. In addition, inert gas may be used as a stripping gas in the hot regenerating zone.

The process is particularly desirable for effecting a desulfurization of gases which have a high heating value and are intended for use in a gas turbine-steam turbine power plant. Such gases having a high heating value may be produced in a manner known per se, e.g., by a gasification of solid fuels.

The gas may be purified by means of various scrubbing solutions, which are selective for  $H_2S$  and which are known per se and may consist, e.g., of physically acting scrubbing solutions, such as methanol, N-methyl pyrrolidone, methyl diethanolamine or also dimethyl ether of polyethylene glycol. The gas is scrubbed in most cases under pressures in the range from 5 to 100 bars and at the known temperatures which are typical of the scrubbing solution employed and lie in the range from  $-80^{\circ}C$  to  $+100^{\circ}C$ . The elementary sulfur is produced under pressures of about 1 to 30 bars or even higher pressures. Pressures of 1 to 10 bars are presently preferred.

Further features of the process will be explained with reference to the drawing. Figures 1, 3, and 4 are flow schemes illustrating various variants

of the process. Figure 2 is a simplified representation of an example of the Claus process plant which may be used in accordance with the invention. Pumps and compressors have been omitted in the drawing for the sake of simplicity and of a clearer arrangement.

In the process illustrated in Figure 1 the gas which is to be desulfurized is fed in line 1 to a scrubbing zone 2, which is supplied with regenerated scrubbing solution through line 3. Purified gas is withdrawn in line 4. Laden scrubbing solution, which contains  $H_2S$  and  $CO_2$ , is supplied in line 5 with a partial pressure relief to a re-absorber 6. The re-absorber consists of a regenerating column, which contains mass transfer-promoting elements known per se, such as liquid- and gas-permeable plates. In the re-absorber 6,  $CO_2$  is substantially stripped off whereas as much  $H_2S$  as possible is kept in the scrubbing solution. For this purpose the re-absorber is supplied at its top through line 8 with regenerated scrubbing solution, which preferentially takes up the sulfur compounds from the rising gases.  $H_2S$ -containing gases from lines 10 and 11 are supplied to the lower portion of the re-absorber and in the re-absorber 6 act as stripping gases to strip off particularly  $CO_2$ . An exhaust gas which is rich in  $CO_2$  is withdrawn from the re-absorber through line 12 and because it has substantially been desulfurized may be combined for most application with the gas from line 4.

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The scrubbing solution from the re-absorber 6 is supplied in line 13 to a heat exchanger 14 and is heated therein and then flows in line 15 to the hot regenerating apparatus 16, in which a reboiler 17 effects the temperature rise which is required for a release of impurities, particularly  $H_2S$ , which are bound to the scrubbing solution. In case of need, a stripping gas may additionally be supplied through the line 18, which is indicated by a dotted line. That stripping gas may consist, e.g., of hydrogen or nitrogen or of a desulfurized exhaust gas.

Regenerated scrubbing solution leaves the hot regenerating zone 16 in line 20 and is cooled in the heat exchanger 14 and in line 21 is recycled to the scrubbing zone 2 and to the re-absorber 6. Exhaust gas which is rich in  $H_2S$  is withdrawn in line 23 from the top of the hot regenerating apparatus 16 and a partial stream thereof is supplied in line 24 to a Claus process plant, which consists of a burner section B and a succeeding hydrogenating section H. Details of the Claus process plant consisting of sections B and H will be explained hereinafter with reference to Figure 2. and it will also be explained that the hydrogenating section H comprises a hydrogenating and/or hydrolyzing stage. Remaining exhaust gas is withdrawn in line 23 from the hot regenerating apparatus 16 and is supplied through a cooler 26 and through line 11 to the re-absorber 6.

It is indicated in Figure 1 that in addition



to the exhaust gas which is rich in  $H_2S$  and conducted in line 24 the Claus process plant is supplied through line 28 with oxygen or air or oxygen-enriched air, that elementary sulfur is withdrawn in line 30, that exhaust gas which contains  $H_2S$  and  $SO_2$  is supplied in line 45 to the hydrogenating section H, and that a part of the  $H_2S$ -containing residual gas from the hydrogenating section is recycled in line 10a for a control of the temperature in the hydrogenating reactor. The scrubbing zone 2, the re-absorber 6 and the hot regenerating apparatus 16 may contain elements known per se, such as plates, for improving the mass transfer.

The Claus process plant which is shown in detail in Figure 2 essentially consists of the burner section B (between items 24 and 40) and the hydrogenating section H (between items 45 and 50) and is operated as follows: Exhaust gas from line 24 and oxygen-containing gas from line 28 are initially supplied to a Claus process burner 31 - or a plurality of burners - provided with an integrated combustion chamber. Details of such a combustor are described in Published German Application 37 35 002 and in U.S. Patent 4,632,819. By the combustion, a gas mixture at temperatures of about 1000 to 2000°C is produced and the oxygen in line 28 is metered to ensure that the mole ratio of  $H_2S$  to  $SO_2$  in the gas mixture lies between 4:1 and 1:1 and preferably at about 2:1.

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The succeeding indirect cooler 32 is provided with a feed water supply line 34 and with a water vapor-withdrawing line 33 and is used to cool the gas mixture below the dew point temperature of sulfur so that elementary sulfur is condensed. That elementary sulfur is delivered in line 30a to a collecting bin 35.

The cooled gas mixture flows in line 37 to a further indirect cooler 38, which is used to improve the yield of elementary sulfur. That elementary sulfur flows in line 30b also to the bin 35. The gas in line 40 is still at temperatures of about 125 to 135°C and is heated in an indirect heat exchanger 43. The thus preheated gas is supplied at temperatures of 180 to 280°C in line 45 to a catalytic hydrogenator 46, which will be supplied through line 46a with hydrogen-containing gases if the hydrogen produced in the combustion chamber 31 is not sufficient. The hydrogenator may be used entirely or in part as a hydrolyzer and is used in known manner mainly to convert  $\text{SO}_2$  to  $\text{H}_2\text{S}$ . Cobalt-molybdenum catalysts may be used, for instance, for that purpose. The gas mixture from the hydrogenator 46 is initially precooled in the cooler 47 and is then fed to a direct cooler 48 for a removal of water. The cooler 48 is supplied with cooling water, which is circulated through an indirect cooler 49. Surplus water is withdrawn in line 50.  $\text{H}_2\text{S}$ -containing residual gas at temperatures of about 20 to 40°C leaves the cooler 48 in line 10 and a partial stream of that residual gas is

recycled in line 10a to the hydrogenator 46 to control the temperature in the hydrogenator. Lines 10a and 46a may alternatively open into line 45. The residual gas flowing in line 10 will be processed further in the manner that is explained with reference to Figures 1, 3, and 4.

The process variants illustrated in Figures 3 and 4 agree with the process of Figure 1 in part so that like reference characters are employed and reference is made to the explanations furnished with reference to Figure 1. In accordance with Figure 3, gas which is to be desulfurized is supplied in line 1a and after it has been mixed with the gas flowing in line 10 is supplied in line 1 to the scrubbing zone 2. In the processes illustrated in Figures 3 and 4 the regenerating apparatus also comprises two regenerating columns 7 and 51, in which the scrubbing solution is partly pressure-relieved and is treated with a stripping gas. The stripping gas for the column 7 comes from line 52 and consists of an exhaust gas which comes from the regenerating column 51 and has flown through the cooler 53. In accordance with Figure 3 a part of the exhaust gas from column 7 is supplied in line 60 to the scrubbing zone 2 and the remainder flows through line 61 to the hydrogenating section H of the Claus process plant. Hydrogen-containing gas is added through line 46a and may be tapped, e.g., from the pure gas flowing in line 4 if that pure gas is

suitable for the purpose.

Stripping gas is supplied in line 18 also to the hot regenerating apparatus 16, and a part of the exhaust gas from the hot regenerating apparatus flows through the control valve 66 and line 67 as a stripping gas to the second regenerating column 51. The scrubbing solution from line 15 flows through the pressure relief valve 15a and subsequently enters the column 51.  $H_2S$ -containing residual gas from the hydrogenating section H is admixed from line 10 to the gas to be purified, which flows in line 1.

The process illustrated in Figure 4 is similar to that shown in Figure 3. In that case the  $H_2S$ -containing residual gas from line 10 is used as an additional stripping gas in the first regenerating column 7 and the entire exhaust gas from that column is supplied through line 60 to the scrubbing zone 2. The entire exhaust gas which is rich in  $H_2S$  and comes from the hot regenerating apparatus 16 is supplied in line 24 to the Claus process plant. Nitrogen, e.g., is used as a stripping gas in the second regenerating column 51 and is supplied in line 62. Hydrogen usually coming from an extraneous source is supplied as a hydrogenating gas through line 46a to the hydrogenating section H. Alternatively, a partial stream of the scrubbed gas in line 4 may be used as a hydrogenating gas.

Example 1

In a processing system as shown in Figure 3, comprising a Claus process plant as shown in Figure 2, a dedusted product gas from the gasification of coal is treated with NMP as a scrubbing solution. Data indicating the rates, pressures and gas components in various lines are apparent from the following tables. All rates, also those of the components, are stated in all examples in kilomoles per hour.

Line	1a	4	5	10	60	61
Rate	10000	10039.4	395.7	192.5	247	119.9
Pressure (bars)	37	36	37	1.1	1.4	1.4

## Components:

CO <sub>2</sub>	1650	1656.4	294	104.3	196.8	95.7
H <sub>2</sub> S	33	-	75	22.7	19.3	9.4
H <sub>2</sub>	4317	4314.4	11	2.8	7.5	3.5
CO	4000	3993.6	15.5	0.4	10.5	5.0
N <sub>2</sub>	-	75	0.2	62.3	12.9	6.3

Line	13	24	46a	52	54	67
Rate	124.4	103.8	4.4	95.6	65.9	37.1
Pressure (bars)	1.5	1.8	36	1.6	1.8	1.8

## Components:

CO <sub>2</sub>	49.2	1.5	0.7	47.7	2	0.5
H <sub>2</sub> S	74.9	46.3	-	28.6	63	16.7
H <sub>2</sub>	-	-	1.9	-	-	-
CO	-	-	1.8	-	-	-
N <sub>2</sub>	0.3	56	-	19.3	0.9	19.9

Nitrogen at a rate of 75 kilomoles per hour is conducted as a stripping gas through line 18. Pure oxygen at a rate of 21 kilomoles per hour is supplied through line 28 to the combustion chamber 31. The laden scrubbing solution in line 5 is at a temperature of  $37^{\circ}\text{C}$ . Elementary sulfur is collected in the bin 35 at a rate of 33 kilomoles per hour. In the hydrogenator 46, a cobalt-molybdenum catalyst is used, which comprises a carrier consisting of activated alumina. A partial stream of the pure gas in line 4 is supplied in line 46a as an additional hydrogenating gas. 35.6 kilomoles of water at  $70^{\circ}\text{C}$  are withdrawn per hour in line 50.

#### Example 2

A processing system as shown in Figure 4 combined with the Claus process plant of Figure 2 is used to process a gas that has been produced by a gasification of coal and is supplied in line 1a. NMP is used as a scrubbing solution. Nitrogen at a rate of 45 kilomoles per hour is supplied as a stripping gas in line 62. The combustion in the combustion chamber 31 is effected with pure  $\text{O}_2$  supplied at a rate of 12.1 kilomoles per hour, and elementary sulfur at a rate of 19 kilomoles per hour is collected in the bin 35. Water at a rate of 24.1 kilomoles per hour is withdrawn in line 50. Further data are stated in the following tables,

in which all rates, also those of the components, are stated in kilomoles per hour.

Line	1	4	5	10	13	24
Rate	10000	10026.8	372.6	9	128.1	27.2
Pressure (bars)	37	36	37	1.4	1.5	1.8
Temperature ( $^{\circ}\text{C}$ )	30	38	36	30	31	

Components:

$\text{CO}_2$	1650	1650	300	-	27	-
$\text{H}_2\text{S}$	19	-	46.3	6.3	100.5	25.3
$\text{H}_2 + \text{CO}$	8331	8331.8	26.3	0.8	-	-
$\text{N}_2$	-	45	-	1.9	0.6	1.9

Line	46a	52	54	60
Rate	6	145.9	27.2	399.4
Pressure (bars)	2.5	1.4	1.8	1.3
Temperature ( $^{\circ}\text{C}$ )	30	30		31

Components:

$\text{CO}_2$	-	27	-	300
$\text{H}_2\text{S}$	-	75.2	25.3	27.3
$\text{H}_2 + \text{CO}$	6	-	-	27.1
$\text{N}_2$	-	43.7	1.9	45.0

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CLAIMS

1. A process of purifying a gas which contains combustible components as well as carbon dioxide and sulfur compounds, particularly  $H_2S$ , wherein the gas is scrubbed in a scrubbing zone with a scrubbing solution, which is regenerated and re-used, wherein the scrubbing solution to be regenerated is pressure-relieved, stripped, and heated in a hot regenerating zone, an exhaust gas rich in  $H_2S$  produced in the hot regenerating zone is processed to form elementary sulfur and a residual gas which contains  $H_2S$ , and the residual gas is contacted with scrubbing solution, characterized in that the exhaust gas which is rich in  $H_2S$  and has been produced in the hot regenerating zone is partly combusted in a combustion chamber with oxygen, oxygen-containing gas or air; a gas mixture which is at a temperature in the range from 1000 to 2000 °C and in which <sup>at least</sup> 50 mole percent of the sulfur supplied to the combustion chamber are contained as elementary sulfur and which also contains the components  $H_2S$  and  $SO_2$  in a molar ratio of 4:1 to 1:1 is produced in the combustion chamber; <sup>the</sup> gas mixture is cooled below the dew point temperature of sulfur; condensed elementary sulfur is removed; the gas mixture is subsequently heated to temperatures of 180 to 280 °C and is directly subjected to a catalytic hydrogenation and/or hydrolysis, whereby the residual content of  $SO_2$  is substantially converted to  $H_2S$ ; and at least part of the gas which



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has thus been treated is contacted as an  $H_2S$ -containing residual gas with scrubbing solution.

2. A process according to claim 1, characterized in that  <sup>$H_2S$ -containing</sup> residual gas which comes from the hydrogenating and/or hydrolyzing stage is supplied to the scrubbing zone.

3. A process according to claim 1 or 2, characterized in that an exhaust gas which is rich in  $H_2O$  and contains  $CO_2$  not in excess of 10 % by volume is supplied to the combustion chamber.

4. A process according to claim 1 or any of the following claims, characterized in that a partial stream of the residual gas coming from the hydrogenating and/or hydrolyzing stage is recycled to a point which precedes the hydrogenating or hydrolyzing stage.

5. A process according to claim 1 or any of the following claims, characterized in that scrubbing solution which comes from the scrubbing zone and contains impurities is partly pressure-relieved in a first regenerating column, which contains mass transfer-promoting elements, a first exhaust gas, which contains  $CO_2$ , is withdrawn from the first regenerating column and is supplied at least in part to the scrubbing zone, the scrubbing solution from the first regenerating column is heated and is partly pressure-relieved in a second regenerating column, which contains mass transfer-promoting elements, partly

regenerated scrubbing solution from the second regenerating column is supplied to the hot regenerating zone, a stripping gas is supplied to the second regenerating column, and a second exhaust gas is withdrawn from the second regenerating column and is supplied as a stripping gas to the first regenerating column.

6. A process according to claim 5, characterized in that  $H_2S$ -containing residual gas which comes from the hydrogenating and/or hydrolyzing stage is supplied as a stripping gas to the second regeneration column.

7. A process according to claim 5, characterized in that nitrogen containing gas is supplied as a stripping gas into the hot regeneration zone and a partial stream of the exhaust gas from the hot regeneration zone is supplied as a stripping gas to the second regeneration column.

8. A process according to claim 5, characterized in that  $H_2S$ -containing residual gas which comes from the hydrogenating and/or hydrolyzing stage is supplied as a stripping gas to the first regeneration column.

9. A process according to claim 1 or any of the following claims, characterized in that a portion of the  $H_2S$ -containing residual gas coming from the hydrogenating and/or hydrolyzing zone is supplied into the combustion chamber.

10. A process according to claim 5 or any of the following claims, characterized in that a partial stream of the first exhaust gas coming from the first regeneration column is supplied to the catalytic hydrogenation and/or hydrolysis zone.

11. A process according to claim 1 or any of the following claims, characterized in that 30 to 80 % of the sulfur which is contained in the exhaust gas which is supplied to the combustion chamber, is gained as elementary sulfur.

12. A process according to claim 1 or any of the following claims, characterized in that the purified gas withdrawn from the scrubbing zone is supplied to a gas turbine-steam turbine power plant.

ABSTRACT

A process of purifying a gas which contains combustible components as well as carbon dioxide and sulfur compounds, particularly  $H_2S$ , in that the gas is scrubbed in a scrubbing zone with a scrubbing solution, which is regenerated and re-used. The scrubbing solution to be regenerated is pressure-relieved, stripped, and heated in a hot regenerating zone. An exhaust gas which is rich in  $H_2S$  and comes from the hot regenerating zone is partly combusted in a combustion chamber with oxygen, oxygen-containing gas or air. A gas mixture which is at a temperature in the range from 1000 to 2000 °C and in which <sup>at least</sup> 30 mole percent of the sulfur supplied to the combustion chamber are contained as elementary sulfur and which also contains the components  $H_2S$  and  $SO_2$  in a molar ratio of 4:1 to 1:1 is produced in the combustion chamber. The gas mixture is cooled below the dew point temperature of sulfur; condensed elementary sulfur is removed; the gas mixture is subsequently heated to temperatures of 180 to 280 °C and is then directly subjected to a catalytic hydrogenation and/or hydrolysis, whereby the residual content of  $SO_2$  is substantially converted to  $H_2S$ . At least part of the gas which has thus been treated is contacted as an  $H_2S$ -containing residual gas with scrubbing solution.